

Passivation phenomenon of low antimony alloys in deep discharge conditions of lead–acid batteries

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Abstract

The effects of the low antimony content and polarisation time on passivation of lead–antimony alloys under deep discharge conditions of the lead–acid batteries were investigated at a potential of +0.7 V versus $\text{Hg} | \text{Hg}_2\text{SO}_4 | \text{K}_2\text{SO}_{4\text{sat.}}$, in a 0.5 M H_2SO_4 solution. Electrochemical techniques and metallographic analyses revealed that the antimony level controls the electric passivation of Pb–Sb alloys, used as positive grid alloys. For low antimony alloys ($\text{Sb} < 0.75 \text{ wt.}\%$), this passivation phenomenon is due to the formation of $\alpha\text{-PbO}$, acting as an electric barrier at the grid surface, and growing through a solid-state diffusion process of O^{2-} anions in a local electric field. Thickness measurements and monitoring of PbO growth by electrochemical impedance spectroscopy have demonstrated, by computation of the diffusion coefficient and the diffusion resistance of O^{2-} anions, that antimony incorporated into the oxide acts as a doping element for its growth. At higher antimony levels, the two-phase alloys (lead matrix + Sb precipitates) promote the formation of a very thin layer of a Sb-rich oxide inhibiting the PbO growth.

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1. Introduction

The deep discharge of lead–acid batteries is one of the main problems in applications to photovoltaic energy storage or electric vehicles, and leads to premature capacity loss of the battery. This phenomenon is due to either the irreversible transformation of a positive active mass (PbO_2) into large lead sulfate crystals, called active mass sulphation (PCL-3), or a progressive swelling and a loss of cohesion of the positive active mass (PCL-2), or the electric passivation of the positive grid alloy used as the electron collector (PCL-1) [1–3]. This passivation phenomenon (PCL-1) called the ‘antimony-free effect’ occurs when Pb–Sb alloys are replaced by PbCa alloys in order to develop maintenance free batteries or valve-regulated lead–acid batteries [4].

For low-cost flooded batteries, lead–antimony alloys are still widely used because of their good charge–

discharge characteristics and their good castability which allows ease of manufacture. However, the decrease in the gas overvoltage during charge due to the high content of antimony is the main drawback of these alloys.

A commonly used method to suppress this negative effect of antimony is to reduce its content in the alloy from 6–8 wt.% down to 1–2 wt.%. The decrease of antimony content would lead to a lowering of water consumption and thus, to a reduction in the maintenance frequency of batteries for stationary applications [5].

The antimony-free effect has been extensively studied on Pb–Ca alloys, and it was attributed to the formation of a poorly-conducting oxide layer between the grid and the active mass, which was identified as tetragonal lead monoxide $\alpha\text{-PbO}$ [6–9]. The formation of $\alpha\text{-PbO}$ is induced by the presence of a lead sulfate layer that acts as a semi-permeable membrane and increases the local pH at the grid | lead sulfate interface up to a value close to 9 [10–12]. Then, the PbO layer grows via a solid state diffusion process of O^{2-} oxygen anions [13,14].

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During the last few years, several authors have shown that a sufficient antimony content in the alloy can suppress the passivation phenomena, because it favours the oxidation of PbO into PbO_n or PbO₂ [15–18].

The purpose of the present work was to obtain a more complete description of the role of this element at a low content, since it seems to have a major effect on the composition of the corrosion layer in deep discharge conditions of batteries. Consequently, the influence of low and very low antimony contents on the passivation of Pb–Sb alloys in sulphuric acid was studied by using quasi-stationary electrochemical techniques (voltammetry, chronopotentiometry and chronoamperometry). Moreover, electrochemical impedance spectroscopy (EIS) contributed to the elucidation of the effect of low antimony contents on the PbO growth. Scanning electron microscopy (SEM) observations and electron probe microanalyses (EPMA) provided further information about the location of antimony in the alloy/oxide system after oxidation.

2. Experimental and methods

The antimony alloys (with wt.% Sb = 0.25, 0.5, 0.75, 1, 2, 3) were formed in the laboratory by melting mixtures of pure elements (99.99 wt.%) in alumina crucibles for 30 min at 600 °C, and casting in a mould of 3 mm thickness at room temperature. Subsequently, these alloys were homogenised by heat treatment at 200 °C for 2 h, then quenched in water. Under these conditions of both cooling rate and heat treatment, the solubility of antimony in the lead matrix was measured by EPMA analyses as about 0.75 wt.%, whereas, beyond this value, the alloys are two-phase (α -lead matrix and β -antimony precipitates).

Electrochemical tests were performed in a three-electrode electrochemical cell connected to an EG&G Princeton 273A potentiostat driven by a computer. EIS experiments were carried out with a Solartron 1255 FRA from 10⁵ to 10^{−1} Hz with a 10 mV amplitude, and the impedance data were fitted with EQUIVCRT software using non-linear least square fit techniques developed by Boukamp [19]. For all the fits, the relative errors on the real and imaginary parts were less than 5% according to the Kramers–Kronig relation [20]. The circular and horizontal working electrode (2.8 cm²) was placed at the bottom of the cell under a Pt-disk electrode. The reference electrode was a K₂SO₄-saturated mercurous sulfate electrode ($E = +0.658$ V versus SHE), and all working electrode potentials are given versus this reference electrode. The electrolyte was a 0.5-M sulphuric acid solution, prepared from Prolabo grade reagent, and maintained at room temperature in all experiments.

The working electrode was mechanically polished with successively finer grades of SiC emery papers up

to 1200, then with colloidal silica dispersed in water (particle size: 0.1 μ m). Metallographic cross-sections were polished in the same way. Samples were finally rinsed with distilled water and ethanol, then dried. Before each experiment and immediately after the sample immersion, the polished lead electrode was reduced by a cathodic current, at -0.1 mA cm^{−2}, until the potential reached the value of -1100 mV corresponding to the beginning of the proton reduction plateau. For all the measurements, the potential scan rate was 1 mV s^{−1}, which was sufficient to maintain the different systems at steady state conditions. The electrochemical tests were performed at $+0.7$ V, which corresponds to the conditions simulating the deep discharge of lead–acid batteries, according to the battery manufacturers. The open-circuit potential measurements were carried out after the electrodes had been maintained at $+0.7$ V for 24 h and the polarisation potential cut off. The thickness of the PbO layers was determined by chronopotentiometry at -0.1 mA cm^{−2} on samples polarised for different times (15 min up to 24 h).

The SEM technique (Hitachi S-2500 equipped with a EDS detector) was applied to determine the morphology and the composition of the surface. The composition of the corrosion layer was analysed by EPMA (Cameca SX-50 apparatus).

3. Results

3.1. Cyclic voltammograms

In order to explore the electrochemical behaviour of the Pb–1.5wt.%Sb alloy containing both the α -phase (Sb-enriched lead matrix) and the β -phase (Sb precipitates) as well as the Pb–0.5wt.%Sb single-phase alloy (α -phase), cyclic voltammograms were recorded at a rate of 1 mV s^{−1} (Figs. 1 and 2). The results are in agreement

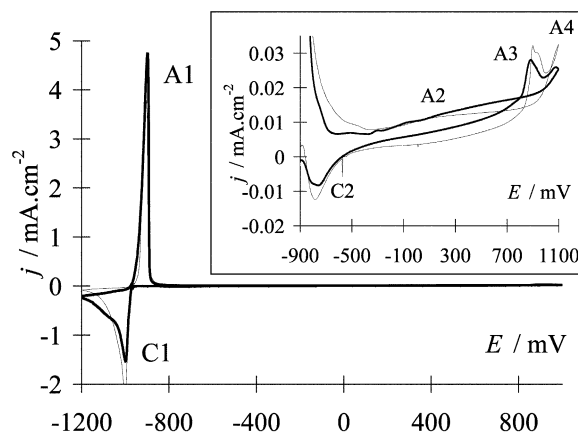


Fig. 1. Voltammogram of pure lead (normal line) and Pb–0.5wt.%Sb (bold line) in 0.5 M H₂SO₄ at 1 mV s^{−1}.

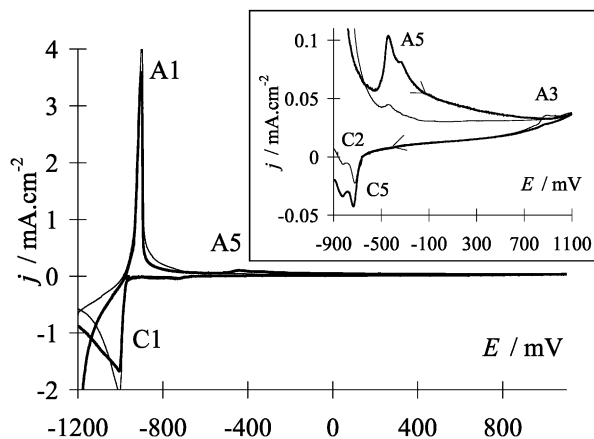


Fig. 2. Voltammogram of Pb-1.5wt.%Sb in 0.5 M H₂SO₄ at 1 mV s⁻¹ (first sweep in bold line, third sweep in normal line).

with Refs. [15,18]. Indeed, during the positive potential sweep, the voltammograms of all the alloys show a well defined A1 peak at -900 mV, which corresponds to the oxidation of lead into PbSO₄, and a current increase A4 at about 1000 mV resulting from the oxidation of water into oxygen (Fig. 1). The lead sulfate is reduced to lead at the peak C1 during the negative sweep. Between A1 and A4, a large passivation plateau appears.

For low antimony alloys (wt.% Sb ≤ 0.75), the increase of the passive current beyond about 0 V ('peak' noted A2 on the Fig. 1) is attributed to the oxidation of lead to lead monoxide PbO, as previously reported on pure lead and other lead alloys [14,21], and PbO is reduced at -850 mV (C2 peak). In the reverse part of the voltammogram (Figs. 1 and 2), the anodic peak (A3) at +900 mV could be attributed to the oxidation of lead to PbO₂ after cracking of the passive layer by the oxygen evolution at high positive potentials [22].

For rich antimony alloys (wt.% Sb > 0.75), the voltammograms present two additional peaks: A5 and C5 (Fig. 2) which are easily attributed to the oxidation of the Sb precipitates to soluble Sb^{III} and Sb^V species. For Pb-1.5wt.%Sb, the progressive dissolution of the antimony precipitates into the electrolyte causes a drastic decrease of the A5 peak intensity after several sweeps (Fig. 2). SEM observations confirm these interpretations (Fig. 3). Indeed, after an oxidation at -900 mV for 15 min (before the A5 peak), the Sb precipitates remain unchanged whereas the lead matrix is covered by lead sulfate (Fig. 3a). On the contrary, after an oxidation at 0 mV for 15 min (after the A5 peak), Sb precipitates are rapidly dissolved into the acid and holes appear at the alloy surface instead of the precipitates. Then, during the negative sweep, the antimony species are reduced at the C5 peak.

3.2. Chronopotentiometry and open-circuit potential measurements

The changes in the open-circuit potential versus time of Pb-1.5wt.%Sb, Pb-2wt.%Sb and pure lead after oxidation for 24 h at +0.7 V in 0.5 M H₂SO₄ are represented in Fig. 4. The same type of evolution is observed for pure lead and all the alloys: the rest potential drops progressively to -550 mV after some hours at open-circuit. In the case of pure lead, this potential value indicates the presence of PbO as previously reported [7,14], but for Pb-Sb alloys, it is difficult to conclude this, as the equilibrium potential values of the Pb/PbO and Sb/Sb₂O₃ redox couples are very close.

Nevertheless, the two oxides can be distinguished by chronopotentiometry at constant current according to the potentiodynamic study, the overvoltages of their reduction reaction being quite different. So, the example of chronopotentiometry of Pb-5wt.%Sb oxidised at 0.7 V for 4 h in H₂SO₄ 0.5 M, shown in Fig. 5, presents several plateaux between -600 and -800 mV corresponding to the reduction of the antimony oxides, the reduction plateau of PbO at -850 mV, and finally the reduction plateau of PbSO₄ at about -1 V.

3.3. Oxide layer analyses

The cross-sections of the two types of corrosion layer observed after 7 days of oxidation at +0.7 V in 0.5 M H₂SO₄ are displayed in Fig. 6. For the low antimony alloys (Pb-0.5wt.%Sb), the corrosion layer is composed of a thick and dense underlayer of α-PbO (Fig. 6a), and a porous superficial lead sulfate layer. Only the PbSO₄ layer is observed on the Pb-5wt.%Sb, with some partially dissolved Sb precipitates at the alloy surface (Fig. 6b).

After the samples were polarised at +0.7 V for several hours (up to 24 h), the oxide thickness was determined by chronopotentiometry at -0.1 mA cm⁻² ($\rho_{\alpha\text{-PbO}} = 9.2$). For 24 h of oxidation at +0.7 V, the PbO thickness increases with antimony content in the alloy until 0.75 wt.%, then falls from 1 wt.%, and remains at very low values for high antimony levels, as reported in Fig. 7. Moreover, the PbO thickness versus the oxidation time at +0.7 V, displayed in Fig. 8, indicates that the growth of the oxide on pure lead and a low antimony alloy is quasi-linear over an oxidation period of 24 h in a first approximation.

In addition, when the oxide thickness was sufficiently large (>1–2 μm) after 7 days of oxidation, EPMA analyses showed that the antimony contents in the oxide layer are slightly smaller than that in the substrate, contrary to the case of the Sn-content in the PbO layer on Pb-Sn alloys [14] (Fig. 9).

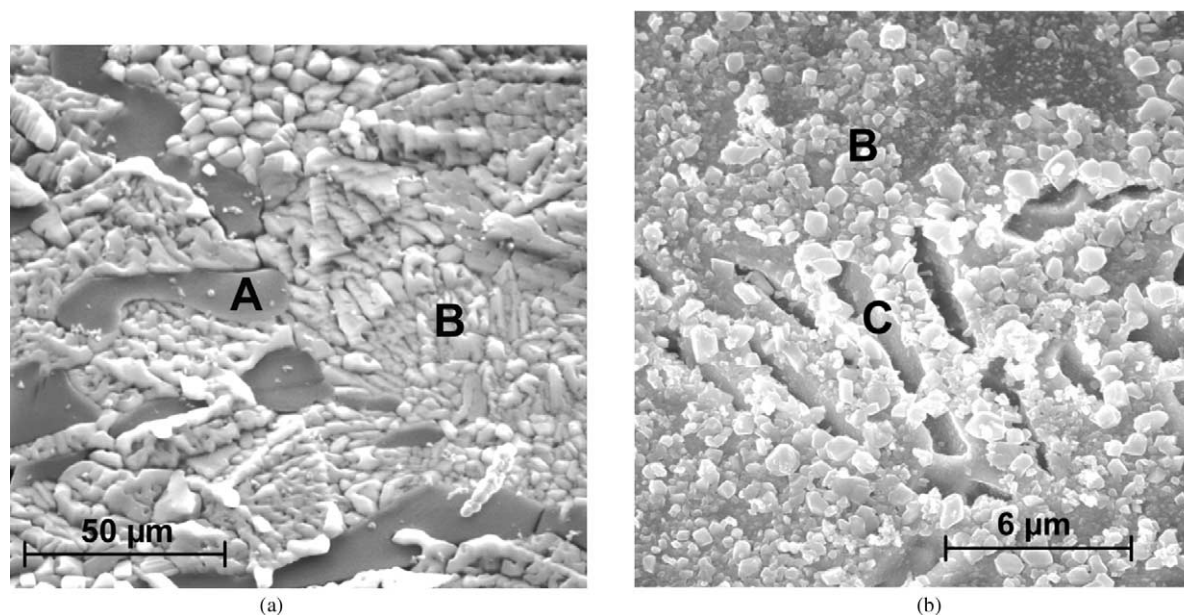


Fig. 3. SEM image of a Pb–5wt.%Sb oxidised for 15 min in 0.5 M H_2SO_4 at -900 mV (a), and at 0 V (b): (1) Sb precipitates, (2) lead matrix covered by PbSO_4 crystals, (3) holes formed after Sb precipitate dissolution.

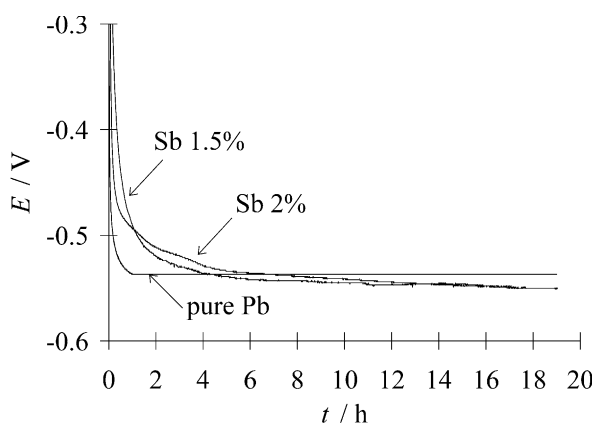


Fig. 4. Evolution of the open-circuit potential of pure lead and different Pb–Sb alloys after polarisation for 24 h at 0.7 V in 0.5 M H_2SO_4 .

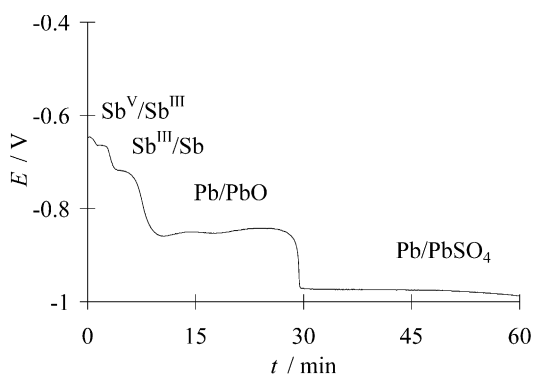


Fig. 5. Chronopotentiometric curve of Pb–5wt.%Sb oxidised for 4 h at 0.7 V in 0.5 M H_2SO_4 . Reduction current density: -0.1 mA cm^{-2} .

3.4. EIS study of PbO growth

In order to study the PbO growth, electrochemical impedance measurements were carried out after every 2 h of oxidation at a fixed potential value equal to 0.7 V, on pure lead and on two low antimony alloys: Pb–0.75wt.% Sb and Pb–0.25wt.%Sb. At this potential, for which a PbOPbSO_4 duplex passive layer is produced, the impedance data profiles of the three alloys are similar and the polarisation resistance ($R_p = \lim_{f \rightarrow 0} [Z(j\omega)]$) increases with the oxidation time, as shown in the example displayed in Fig. 10.

According to the work of Varela et al. [23] in 5 M H_2SO_4 , the outer PbSO_4 layer is dense and compact, so its contribution to the impedance spectra is identified by a capacitive loop at low frequencies. However, in 0.5 M H_2SO_4 , previous ellipsometric studies have shown the high porosity of this PbSO_4 layer [12]; therefore, its electric contribution can be neglected for this sulphuric acid concentration. Consequently, the electrochemical interface can be represented by a simple equivalent circuit (Fig. 11). The choice of this circuit was a compromise between a reasonable fitting of the experimental values and a good description of the electrochemical system by keeping the number of circuit elements at a minimum. This equivalent circuit is composed of:

- R_e the electrolyte resistance of sulphuric acid,
- R_2 and C_{SC} respectively associated with the electronic resistance of the oxide and the space charge of the semiconductor PbO oxide,

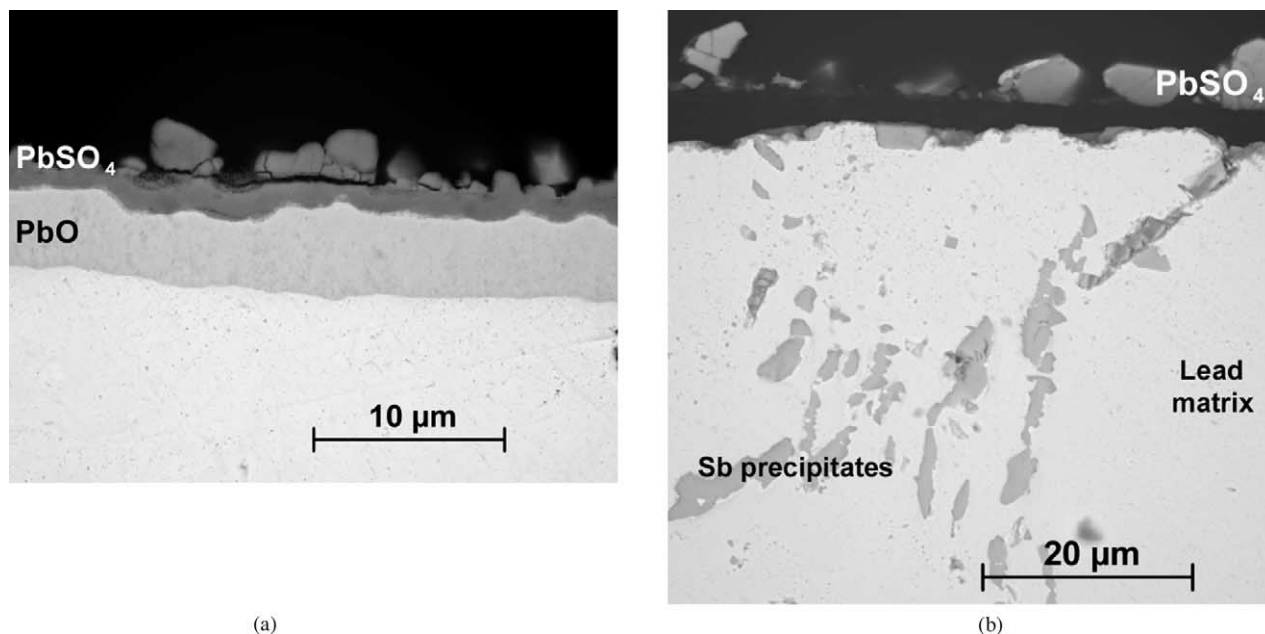


Fig. 6. Metallographic cross-section of a Pb–0.5wt.%Sb (a), and Pb–5wt.%Sb (b) oxidised at 0.7 V in 0.5 M H₂SO₄ for 7 days.

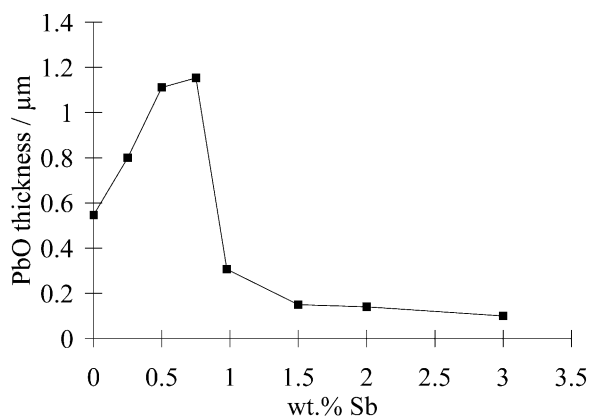


Fig. 7. Thickness of the oxide layer versus antimony content in alloys after polarisation of lead alloys for 24 h at 0.7 V in 0.5 M H₂SO₄.

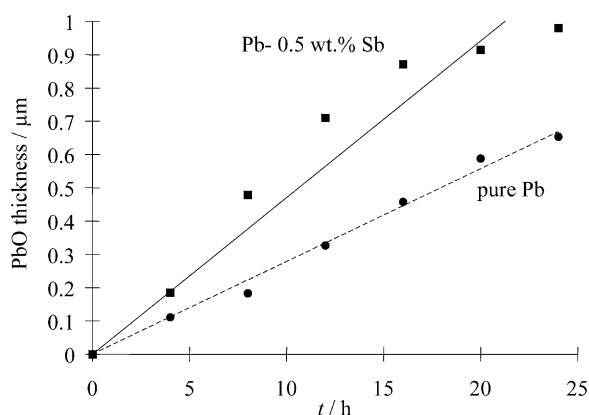


Fig. 8. Growth kinetics of the PbO layer for pure lead and Pb–0.5 wt.%Sb polarised at 0.7 V.

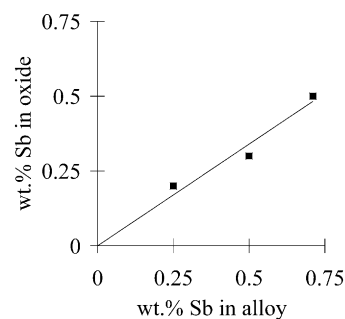


Fig. 9. Antimony content in oxide versus antimony content in the corresponding alloys after an oxidation of 7 days at 0.7 V in 0.5 M H₂SO₄.

- and Z_w a Warburg-like component related to the diffusion of a particle in a region of length l corresponding to the thickness of the passive oxide film.

In the case of the Pb/PbO system, Pavlov [24] has proposed a solid-state mechanism for the growth of the PbO layer and, recently, experiments with ¹⁸O as a tracer showed that the oxide growth is mainly due to the solid-state diffusion of interstitial O^{2–} anions in the α-PbO layer [13]. According to Macdonald and coworker [20,25], the diffusion of a charged particle in a finite length region of an unsupported electrolyte, which is the case of solid-state diffusion, can be modelled by the following expression:

$$Z_w(j\omega) = R_d \left(j\omega \frac{l^2}{D} \right)^{-0.5} \tanh \left[\left(j\omega \frac{l^2}{D} \right)^{-0.5} \right]$$

where l is the thickness of the oxide layer, D the

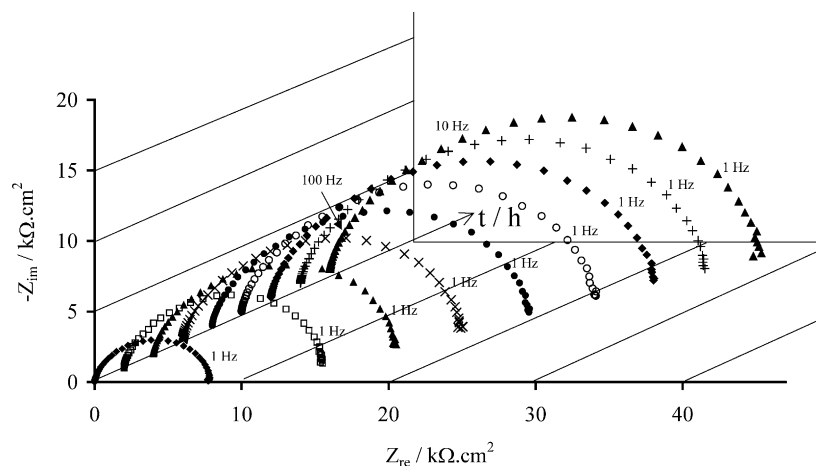


Fig. 10. Nyquist plot of impedance data measured at 0.7 V every 2 h of oxidation at 0.7 V in 0.5 M H₂SO₄ of a Pb–0.25wt.%Sb alloy.

diffusion coefficient of O^{2−} anions; R_d the diffusion resistance of the oxide (i.e. $R_d = \lim_{f \rightarrow 0} [Z_w(j\omega)]$), ω the angular frequency ($j^2 = -1$). R_d can be expressed as follows, assuming an ideal solution in an ionic solid:

$$R_d = \frac{RT}{z^2 F^2} \times \frac{l}{D c_{O^{2-}}^0}$$

where $c_{O^{2-}}^0$ is the O^{2−} concentration at the electrolyte | oxide interface and z the charge of O^{2−} anions.

R_D and (l^2/D) values were computed from the fitting data by the EQUIVCRT software. Then to determine the values of D , the growth of PbO thickness l was assumed to be linear versus the oxidation time taking the results shown in Figs. 7 and 8 into account.

Fig. 11a and Table 1 present the fitting results for the Pb–0.25wt.%Sb alloy. It should be noted that the electrolyte resistance R_e is very low about 2–3 Ω cm² and remains constant during the oxidation. The R_2 electric resistance of the PbO film increases with time, which corroborates the increase of its thickness. The order of magnitude and the change of R_2 are almost identical for all the samples.

Fig. 12 represents the C_{SC} , R_d and D curves versus time of the PbO layer formed on pure lead and two low-Sb alloys at 0.7 V in 0.5 M H₂SO₄. The space charge capacity C_{SC} of the oxide decreases and remains constant after 10 h of oxidation, which means that the space charge region reaches an equilibrium state. Moreover, the increase of C_{SC} with addition of antimony in alloys indicates that the space charge concentration increases in the semiconductor oxide (Fig. 12a), which can be correlated with the increase of the Sb content in the oxide (Fig. 9). In the same way, the diffusion resistance of O^{2−} anions, R_d , is closely dependent on the Sb content and increases with the oxidation time, so with the oxide thickness. Indeed, R_d is drastically reduced in the presence of antimony in alloys (Fig. 12b).

In addition, the easier ionic diffusion in PbO formed on low Sb alloys is also indicated by the diffusion coefficient D value under these oxidation conditions. Indeed, the computed D values for all the samples seem to be almost constant with the oxidation time, and show that antimony improves the solid-state ionic diffusion in the oxide by increasing the D value by 1–2 orders of magnitude (Fig. 12c).

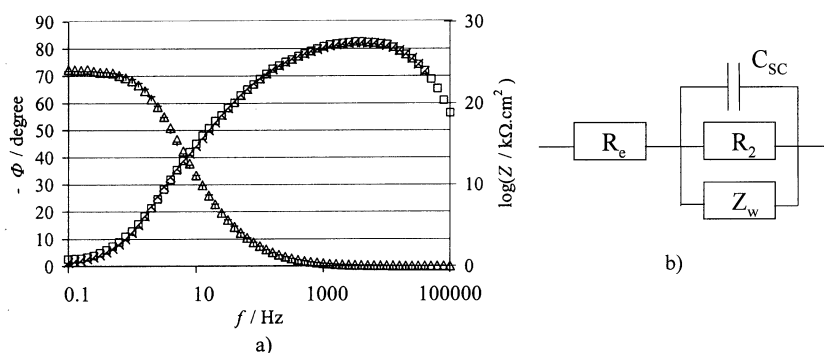


Fig. 11. (a) Bode plots ((□, ×) bode phase; (Δ, +): bode modulus) for fitting results for Pb–0.25wt.%Sb alloy at 0.7 V in 0.5 M H₂SO₄ after 12 h of oxidation: (Δ, □) experimental data; (×, +) data fit result. (b) Equivalent circuit used to fit the impedance data measured during the PbO growth.

Table 1

Example of fitting values computed using the equivalent circuit (Fig. 11b) from EIS data recorded during the oxidation of Pb–0.25wt.%Sb alloy at 0.7 V in 0.5M H₂SO₄

Oxidation time/h s ^{-1/2}	$R_e/\Omega \text{ cm}^2$	$C_{SC}/\mu\text{F cm}^{-2}$	$R_2/\text{k}\Omega \text{ cm}^2$	$R_d/\text{k}\Omega \text{ cm}^2$	$\bar{I}/D$
2	2.5	0.75	9.8	37.2	0.102
4	2.6	0.62	18.2	50.8	0.149
6	2.6	0.60	22.6	59.4	0.176
8	2.7	0.58	26.2	67.4	0.201
10	2.7	0.56	29.3	80.0	0.239
12	2.7	0.35	32.7	89.7	0.267
14	2.8	0.53	34.9	101.6	0.313
16	2.8	0.50	37.2	103.7	0.308
18	2.9	0.47	39.4	110.6	0.316

4. Discussion

From the results obtained through this study, the PbO growth responsible for the passivation phenomenon on low antimony alloys in sulphuric acid depends strongly on the Sb content. Indeed, two types of alloys can be distinguished according to their electrochemical behaviour.

For alloys containing α and β phases (more than 0.75 wt.% of antimony in this study), their behaviour under deep discharge conditions is closely related to the presence of an Sb-rich eutectic structure at the grain boundaries of alloys, as is noted on the metallographic

cross-sections of a Pb–5wt.%Sb alloy (Fig. 3). During the first oxidation step, Sb precipitates are preferentially dissolved, then the alloys are covered by a thin layer of an Sb-rich oxide, which seems to inhibit the O²⁻ diffusion in the metal and suppresses the growth of a thick PbO layer. According to the chronopotentiometric experiments (Fig. 5) and to the conclusions of some authors [15,22], Sb₂O₃ or a PbO–Sb₂O₃ mixed oxide seems to be the major component of this thin passive layer. Recently, Yasukawa et al. [26] have shown that additions of antimony to the positive active mass can inhibit the passivation phenomenon of PbCa grids during deep discharge cycling. Their results revealed

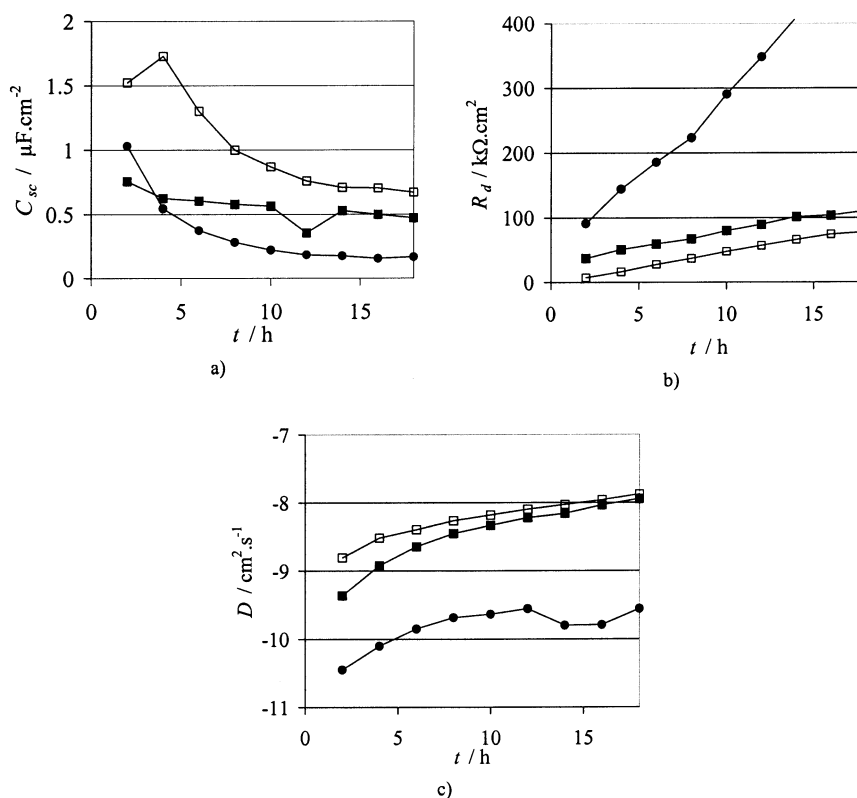


Fig. 12. (a) C_{SC} ; (b) R_d and (c) O²⁻ diffusion coefficient D calculated from the fitting results of impedance data for pure and two low-Sb alloys versus the oxidation time at 0.7 V in 0.5 M H₂SO₄: (—□—) Pb–0.75wt.%Sb; (—■—) Pb–0.25wt.%Sb; (—●—) pure lead.

that antimony was mainly located in the corrosion layer, which confirms the role of antimony in the inhibition of PbO growth.

Contrary to two-phase Sb alloys, the passivation phenomenon on alloys containing 0 to 0.75 wt.% of antimony is characterised by the growth of a thick and dense layer of α -PbO, which presents approximately the same Sb content as the alloys. The oxide growth is almost linear with oxidation time, and its thickness increases with antimony level in the metal for the same oxidation time. Previous studies performed in our laboratory have shown that the solid state diffusion of O^{2-} interstitial oxygen anions under the local electric field in α -PbO is responsible for its growth on lead [13]. Indeed the large growth rate of PbO on pure lead, about $0.6 \mu\text{m day}^{-1}$, can be explained by the important diffusion coefficient of the oxygen anion, about $10^{-10} \text{ cm}^2 \text{ s}^{-1}$, computed from the EIS data (Fig. 12). This D value has the same order of magnitude as the diffusion coefficient for lithium in intercalation compounds such as Fe–V mixed oxide [27] or tungsten bronze [28].

Consequently, by adding Sb^{III} or Sb^{V} cations to the α -PbO structure, a defect equilibrium in this oxide can be written according to the Kröger–Vink notation, as follows: $\text{Sb}_2\text{O}_3 \rightarrow 2\text{Sb}_{\text{Pb}} + \text{O}_i'' + 2\text{O}_0$. So, an addition of antimony provokes an increase of O^{2-} interstitial concentration, then a greater oxygen flux towards the metal and an increase of the PbO growth rate. This results in the increase of the diffusion coefficient of O^{2-} anion in the PbO structure and a decrease of the diffusion resistance, as is demonstrated using the EIS data (Fig. 12).

5. Conclusion

Finally, according to the effect of the antimony content in lead alloys, this element plays a major role in the passivation phenomenon in the PbO growth in sulphuric acid medium. It is noteworthy that, at a low concentration in solid solution in the lead matrix, the effect of tin (previously studied [14]) and antimony on the PbO growth are similar: Sn^{IV} and Sb^{III} or Sb^{V} act as doping elements on the PbO growth, until the appearance of free Sn and Sb precipitates in the alloys. The inhibition of PbO growth seems to be closely linked to an activity effect of these active element (Sb or Sn) in the metal.

Consequently, for industrial applications of lead–acid batteries, it is necessary to achieve a sufficient Sb

content in the grid alloy which depends on the conditions of the process (casting conditions and cooling rate), in order to maintain some Sb precipitates at the metal surface and thus to avoid PbO growth during the cycle life of batteries.

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